ELECTROLYTIC AND PHOTOMETRIC STUDIES OF CERIUM SOLUTIONS

BY
ARTHUR EDWIN KOTT
S.B., University of Chicago, 1931
S.M., University of Chcago, 1932

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SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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CHEMISTRY IN THE GRADUATE SCHOOL OF
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INTRODUCTION

Acid solutions of compounds of tetravalent cerium are important in analytical chemistry as standard oxidizing agents.[1, 2] In recent years Smith and co-workers[3-7] have shown that high oxidation potentials are obtained in nitric or perchloric acid solutions; this simplifies many procedures, and makes possible stoichiometric oxidations of many organic compounds.

There has always been considerable difficulty involved in the preparation of cerium solutions for use as analytical reagents, by strictly chemical methods. It has now been found that electrolytic oxidation of cerous salts provides a convenient and satisfactory method for the preparation of these solutions.

The two main purposes of the present work are:

1. To study the composition of acid solutions of compounds of tetravalent cerium, in the concentration range in which these are usually employed in analysis, with especial reference to the extent and nature of complex ion formation; and

2. To study the conditions for the practical electrolytic preparation of cerium solutions to be used as standard oxidizing agents.

EXPERIMENTAL

The apparatus used for electrolysis consisted of platinum electrodes, a motor stirrer for mixing the electrolyte, storage batteries, ammeter and voltmeter, and a carbon disk rheostat.

Analyses were made by titrations, with standard ferrous sulfate solution, of portions withdrawn from the solution during electrolysis. For determination of the total cerium content, the persulfate oxidation method of Willard and Young[8] was used.

It was found that the electrolysis, without a partition in the cell, of acid solutions of cerous salts, and of compounds of tetravalent cerium, reached a state of equilibrium, after which further passage of the current did not change the percentage of total cerium which was in the oxidized condition. The effects of cerium concentration, of anode to cathode surface ratio, and of acid concentration, were investigated.

Increase in the total cerium concentration increased the percentage oxidation attained. The use of high anode to cathode surface ratios (200 to 1 and 500 to 1), instead of equal electrode surfaces, also gave a higher percentage oxidation.

The effect of varying the concentration, from one to eight molar, of sulfuric, nitric, and perchloric acids, was studied with equal electrode surfaces, and also with a 500 to 1 ratio of anode to cathode surface. The total cerium concentration was 0.025 N. With equal surfaces, the percentage oxidation which was reached in sulfuric acid decreased from 46.3% to 44%, with change in acid molarity from 1 to 5; then increased to 47.8% at 8 molar. In nitric acid there was no oxidation with equal electrode surfaces. In perchloric acid the percentage oxidation increased from 41% at one molar acid to 48% at 8 molar.

At the high ratio the same kind of variations (over a 2 to 5% range) were found in sulfuric and perchloric acids, the highest values being 98.8% at one molar sulfuric acid, and 98.2% at 8 molar perchloric acid. In nitric acid the percentage oxidation with this 500 to 1 ratio increased from 54.8% at one molar acid to 89.2% at 8 molar.

The color of oxidized cerium solutions, at constant cerium concentration, was studied at various acid molarities by measurements of the light absorption in a photoelectric photometer. In each acid, over the range of molarities studied, the variations in light absorption showed the same directions of change as the variations in percentage oxidation in electrolysis.

Electrolytic preparations conducted on a larger scale (2 liters of 0.5 N cerous solutions) showed that almost complete oxidation (99.2-99.9%) could be obtained, in 1 M sulfuric acid, 8 M nitric acid, or 8 M perchloric acid, with platinum electrodes. The anode to cathode surface ratio was 200 to 1, and the electrolyses were conducted at 10 amperes and 3.5 volts.

Use of a graphite anode was found practical in sulfuric acid solutions, at an anode to cathode surface ratio of 100 to 1. 95% oxidation was reached. In the other acids the graphite electrodes were considerably attacked, and the percentage oxidation was much lower.

Stability studies, with oxidized cerium solutions in contact with platinum and carbon, were conducted for periods up to 69 days. With bright platinum there was very slight reduction; contact with platinum black or with graphite caused some reduction in sulfuric acid solution,

and brought about a rapid reduction in nitric and in perchloric acid solutions. With these two acids, the normality fell to about half of its original value in two days, and in 35 days the solutions were almost completely reduced. The rate of reduction was somewhat faster, in both of these acids, with platinum black, than it was with graphite. In all cases the rate of reduction decreased as the concentration of the tetravalent cerium became less.

DISCUSSION

Equilibria among various complex ions of tetravalent cerium, which contain different numbers of water, hydroxyl, and acid anion groups, are postulated to explain the experimental data. Increase in acid concentration is considered to convert hydroxyl groups into water groups, and to replace water groups by acid anion groups. The complex ions which contain sufficient water groups are positively charged; variations in the concentration of these, which can be reduced at the cathode, are assumed to account for the changes in the percentage oxidation reached. Displacement of equilibria in the direction of complexes containing fewer water groups and more acid anion groups is assumed to increase the color.

In a simplified form, these equilibria may be represented somewhat as follows, for increasing molarity of acid:

$$Ce\ (H_2O)_3\ (OH)_3\ (SO_4)^{-1} = Ce\ (H_2O)_5\ (OH)\ (SO_4)^{+1} = Ce\ (H_2O)_2\ (SO_4)_3^{-2} = Ce\ (SO_4)_4^{-4}$$

$$Ce\ (H_2O)_4\ (OH)\ (NO_3)^{+2} = Ce\ (H_2O)_2\ (OH)\ (NO_3)_3^{0} = Ce\ (OH)\ (NO_3)_5^{-2} = Ce\ (NO_3)_6^{-2}$$

$$Ce\ (H_2O)_3\ (OH)_2\ (ClO_4)^{+1} = Ce\ (H_2O)_2\ (OH)\ (ClO_4)_3^{0} = Ce\ (H_2O)\ (ClO_4)_5^{-1} = Ce\ (ClO_4)_6^{-2}$$

Other similar complex ions are undoubtedly also present, but the general trends in color and in electrolytic oxidation, and the displacements due to varying acid molarity which cause them, may be followed with the ions represented.

Smith and Getz[3] found wide variations in the oxidation potential of tetravalent cerium, with change from one acid to another, and at various concentrations of the same acid. These potentials are affected

by the nature of complex ion formation, and it may be assumed that not only the change from one kind of complex ion to another, as the acid present is changed, but also the shift in equilibria among different complexes, in the same acid, should change the value of the potential.

In the electrolytic preparation of cerate solutions, the current efficiency, or effectiveness of use of the electric current, with platinum electrodes, was 95 to 98%, for oxidation up to about 95% complete; above this the current efficiency fell off rapidly. With graphite anode the current efficiency was lower, probably because hydrogen peroxide, formed at the anode, reduced some of the oxidized cerium during the electrolysis.

The reduction of oxidized cerium solutions in contact with platinum black or carbon is considered to be due to an oxidization of water, with formation of oxygen gas. The catalytic effect of the surfaces present is related to the low overvoltage of oxygen on these surfaces. Under the conditions used for electrolytic preparation, with electrodes of bright platinum in all three acids, or with graphite anodes in sulfuric acid, reduction from this source is negligible, in the time required for the electrolysis.

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VITA

Arthur Edwin Kott was born in Chicago, on May 29, 1909. He attended public elementary and high schools in Chicago, and was a student at Crane Junior College, Chicago, for two years. In 1929 he entered the University of Chicago. He received the S. B. degree from that institution in 1931, and the S. M. degree in 1932. He was next employed for five years by E. A. Siebel and Co., Chicago, analytical and consulting chemists. He held the position of research chemist in this company for two years, and was chief chemist of the laboratory for two years. He also taught general chemistry and quantitative analysis in the Bureau of Bio-Technology, operated by E. A. Siebel and Co. In 1938 he entered the Graduate School of the University of Illinois. He was an assistant in chemistry from February 1939 to June 1940. His publications are:

1. Johnson, Morey, and Kott, "Nitrogen Compounds of Germanium," J. Am. Chem. Soc., **54,** 4278 (1932).
2. Siebel and Kott, "Determination of Specific Gravity," J. Assoc. Official Agr. Chem., **20,** 535 (1937).
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